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The Valence Bond Study for Benzenoid Hydrocarbons of Medium to Infinite Sizes

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The ground-state energies of polyacenes and polyphenanthrenes are obtained with the density-matrix renormalization group method from finite up to infinite lengths under the classical valence bond theory. In comparison with the exact valence bond results, numerical errors of retaining various numbers of states are all less than 10^{-5} J. Meanwhile, the linear equations in terms of the chain length are deduced for the ground-state energies of these two homologous series. And the energy gaps between the lowest singlet and triplet states (S−T gap) are also evaluated. On the other hand, the relative local hexagon energy converges as the chain length increases, and leading to an effective conjugated length of $n = 12$ for polyacene and polyphenanthrene.

1. Introduction

The modern valence bond (VB) theory has been developed to explore the electronic structures, reactivity, aromaticity, and many other properties of small benzenoids in recent years.[1−6] With the increase in the sizes of these conjugated systems, the VB theory, a basic many-electron approach, will encounter a fundamental problem of rapid increase in the dimension of the covalent space. How to overcome this obstacle has been a main subject for the scientists.[5−7] So far, conjugated systems with no more than 30 π-electrons can be solved exactly on typical workstations.[4c] Meanwhile, approximate schemes limited to the subspace spanned by the Kekulé structures or taking into account the single and double excitations are now applied to systems as large as fullerenes,[9] where the dimension of the energy matrixes in this approximation are kept under 10^6.

The density-matrix renormalization group (DMRG) method introduced by White has been extremely successful in solving the many-electron models for one-dimensional systems,[10] especially the Heisenberg model[10−14] and the Hubbard model.[15−17] However, although in extension to quasi-one-dimensional or two-dimensional systems, the exponential decrease of the numerical precision with the increase of the system width makes this method rapidly impractical. This “exponential disaster” makes the method inaccessible to most systems of chemical interests.[18−20] Some efforts have been devoted to solve this problem. Use of the frontier molecular orbitals instead of all atomic orbitals in each block space is a good scheme to implement the DMRG calculation for the quasi-one-dimensional and two-dimensional systems.[6,8] But the numerical precision of this technique is unsatisfactory in most cases. To get more precise results, another way has been suggested to deal with the two-dimensional system by choosing the blocks carefully.[21,22] The “careful choosing” including the selection of the starting blocks and the blocks added thereafter plays the important role in implementing DMRG calculations. In this article, we introduce a scheme of choosing the suitable blocks for cata-condensed aromatic systems, which stimulates us to look for satisfactory numerical results in DMRG computations. We perform DMRG calculations on VB energies of the ground and the first triplet states for two series of polycyclic aromatic hydrocarbons (PAHs): polyacene (Pac) and polyphenanthrene (Pph) of arbitrary lengths defined by the number of constituent hexagons, n, or carbon atoms $N = 4n + 2$.

This article is organized as follows. The methodology is presented in the first part. After an outline of VB model is presented, the infinite DMRG method and the strategy of block selection are introduced. Then the index of the relative local hexagon energy (RLHE) currently used for specifying the benzene character of hexagons in benzenoid hydrocarbons is pursued.[5] In the second part, our numerical calculations give the ground-state energies, singlet−triplet energy gaps, and RLHE values of Pac and Pph to analyze the regularities in relationship to the chain length of PAHs up to infinity. Finally, a short discussion about the perspective for the application of DMRG in chemistry is emphasized.

2. Methodology

2.1. VB Model. The classical VB model used in conjugated systems is currently formulated in the Heisenberg form,

$$H = J\sum_{i\sim j}\left(2\mathbf{S}_i\mathbf{S}_j - \frac{1}{2}\right) \tag{1}$$

where $i \sim j$ specifies the nearest-neighbor or bonded atom pairs for the π-electron skeleton of the molecule, S_i, the spin operator of the ith site and J is an (positive) exchange parameter. The wave function can be written as a linear combination of Slater determinants of atomic states limited to the subspace of conserved z-component of total spin, namely,

$$\psi = \sum_i c_i\varphi_i \tag{2}$$

The energy matrix entries between two Slater determinants are easily evaluated, where the diagonals are specified by

$$\langle\varphi_k|H|\varphi_k\rangle = -(\text{number of spin-alternation for bonded pairs in } \varphi_k) \tag{3}$$

and off-diagonals take values below

$$\langle\varphi_k|H|\varphi_l\rangle = 1 \text{ or } 0 \tag{4}$$

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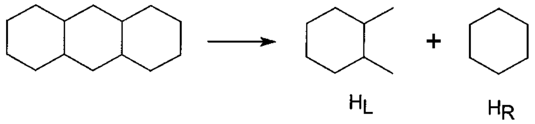
CHART 1



in which 1 results only if the two Slater determinants differ by just one spin exchange on a specified bonded pair, otherwise, 0 results. Thus, the main task of the VB model is the diagonalization of the energy matrix. For the small benzenoids, such as benzene, naphthalene, the classical VB theory, which accounts for the nearest-neighboring interaction approximation, were improved by Malrieu and co-workers with the fourth- and sixth-order corrections.[23a,23b] Meanwhile, as the size of the system increases, the effect of these higher-order corrections will remarkably decrease.[23c,39] Thus, for large or extended benzenoids, the classical VB model will be generally applicable. Because we are interested in the systematic study of the finite up to infinite size systems, the higher-order corrections will not be considered in this article.

2.2. DMRG Method. A system of a given size, referred to as the superblock, is divided into two pieces, the system block and the environment block. We diagonalize the superblock and focus on a particular eigenstate of the system. Then we project this eigenstate from the space of superblock into the system space and define the reduced probability density matrix ($\rho_{ii'}$) = ρ. If ψ is such a state of the superblock,

$$|\psi\rangle = \sum_{ij} \psi_{ij} |i\rangle |j\rangle \tag{5}$$

where $|\iota\rangle$ labels the states of the system block, and $|j\rangle$ labels the states of the environment block, we have the matrix entries of ρ,

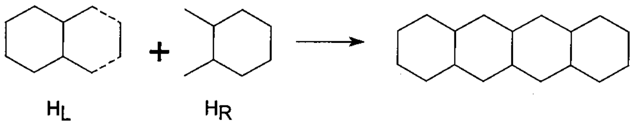
$$\rho_{ii'} = \sum_{j} \psi_{ij} \psi_{i'j} \tag{6}$$

The diagonalization of ρ leads to a set of eigenvalues ω_α and eigenvectors u^α. According to the definition of the density matrix, the states corresponding to larger eigenvalues of density matrix ρ are the more probable configurations of the system block. Therefore, we discard those but the m largest eigenvalues and associated eigenvectors. Accordingly, the matrix representation of operators (such as H) is transformed into $H' = OHO^+$ of dimension m, producing a new system block. O is rectangular, specified by the m highest eigenvectors of ρ as columns, O^+ is the transfer of O.

After the transformation, one adds a block to the starting block to form a superblock of larger size, which is again diagonalized to obtain the particular states. Repeating this treatment recursively, we can obtain the targeted eigenvalues and eigenvectors for PAHs of various sizes. Because the width of the system significantly influences the numerical accuracy, we must keep the number of adding states as small as possible in comparison with the retaining states at each step in calculation.

Let's discuss Pac for illustration. We begin with anthracene. In the first step, we calculate the ground state of anthracene by using the standard method. Then we divide the anthracene into two parts, L (left) and R (right) shown in Chart 1, and form the density matrix of the left block which is diagonalized for choosing m eigenvectors with the largest eigenvalues to induce a new system block, $H'_L = OH_LO^+$. In the next step, we form a larger superblock with H'_L, an extra ethylene (added block), and H'_R, the reflection of the left block as shown in Chart 2.

CHART 2



We diagonalize the combined blocks above and get the ground state of naphthacene. Repeating similar steps described above, we will obtain results for the ground states of higher members of polyacenes one by one. In a similar way, one can deal with other PAHs, for example, Pph.

Before applying this method to the larger systems, we still need to validate the numerical results of this method in reference to the exact values available to the quasi-one-dimensional systems investigated. It is also interesting to evaluate the effective conjugated length where molecular properties saturate and become independent of the propagation of chain length. By extrapolation, the asymptotic behavior of the long-chain PAH can also be reliably estimated.

2.3. Relative Local Hexagon Energy. Similar to Herndon-Ellzey's definition of local aromaticity,[24] the index RLHE used by our group for specifying the local aromaticity per hexagon,[5] is defined as follows:

$$\text{RLHE} = (\text{the ground-state energy of local hexagon})/ \\ (\text{the ground-state energy of benzene}) \tag{7}$$

where the ground-state energy of local hexagon E_r satisfies the following equality in the VB scheme,

$$E_r = -2J \sum_{i\sim j} P_{ij} \tag{8}$$

and P_{ij} represents the probability of atom pair i and j in the ground states,[25] $i\sim j$ means the summation runs over the six bonds in the hexagon. P_{ij} takes

$$P_{ij} = \langle\psi|\frac{1}{2}(a_i^+ a_{\bar{j}}^+ - a_{\bar{i}}^+ a_j^+)(a_{\bar{j}} a_i - a_j a_{\bar{i}})|\psi\rangle \tag{9}$$

where $a_{\bar{i}}^+$ and a_i represent the creation operator for down-spin and annihilation operator for up-spin on atom i, respectively.

3. Results and Discussion

3.1. Numerical Precision. In Tables 1 and 2, we list the lowest singlet and triplet energy of Pac and Pph from $n = 3$ to $n = 6$ calculated by the DMRG method and the exact-diagonalization method, respectively.[3,5] Tables 3 and 4 not only cover the lowest singlet and triplet energy of Pac and Pph from $n = 3$ to $n = 10$ with the DMRG method and exact-diagonalization method, but the results with direct diagonalization of the Kekulé subspaces in the fifth column, the ground energy increments of the neighboring members of the homologue series in the sixth column, the average ground-state energies per electron in the seventh column, and the singlet−triplet energy gaps in the eighth column. First, let us discuss the relationship between the number of retaining states and the numerical precision. The DMRG calculations were implemented under the truncation with $m = 128$, 256, and 512 states in each iteration for comparison of numerical convergence. It is obvious that the more states that are retained in the truncation, the better is the numerical precision. For the least m of 128 states adopted in Table 1, the numerical errors between DMRG and exact values are less than 10^{-5} J for the ground state and 10^{-3} J for

TABLE 1: The Comparison of the Ground-State and First Excited State Energies (in Units of *J*) of Pac between the DMRG Method of Different States Retained and the Exact-Diagonalization Method

	$m = 128$		$m = 256$		$m = 512$		exact	
n	singlet	triplet	singlet	triplet	singlet	triplet	singlet	triplet
3	−21.45050	−20.67185	−21.45050	−20.67185	−21.45050	−20.67185	−21.45050	−20.67185
4	−27.85818	−27.22081	−27.85819	−27.22240	−27.85819	−27.22240	−27.85819	−27.22240
5	−34.26649	−33.72248	−34.26652	−33.72355	−34.26652	−33.72356	−34.26652	−33.72357
6	−40.67563	−40.19478	−40.67566	−40.19574	−40.67566	−40.19576	−40.67566	−40.19577

TABLE 2: The Comparison of the Ground-State and First Excited State Energies (in Units of *J*) of Pph between the DMRG Method of Different States Retained and the Exact-Diagonalization Method

	$m = 128$		$m = 256$		$m = 512$		exact	
n	singlet	triplet	singlet	triplet	singlet	triplet	singlet	triplet
3	−21.52250	−20.64475	−21.52250	−20.64475	−21.52250	−20.64475	−21.52250	−20.64475
4	−27.99497	−27.21202	−27.99497	−27.21658	−27.99497	−27.21658	−27.99497	−27.21658
5	−34.47082	−33.74987	−34.47083	−33.75244	−34.47083	−33.75249	−34.47083	−33.75256
6	−40.94598	−40.27017	−40.94598	−40.27229	−40.94598	−40.27237	−40.94598	−40.27243

TABLE 3: Ground-State and First Excited State Energies (in Units of *J*) of Pac as a Comparison of the DMRG Method (m = 256) with Other Methods

n[a]	E_S(DMRG)	E_T(DMRG)	E_s(exact)[b]	E_T(exact)[b]	E_0(K)[c]	ΔE_s	E_s/N[d]	$\Delta E_{S\rightarrow T}$
3	−21.45050	−20.67185	−21.45050	−20.67185	−20.15000		−1.53218	0.77865
4	−27.85819	−27.22240	−27.85819	−27.22240	−25.82999	−6.40769	−1.54768	0.63579
5	−34.26652	−33.72355	−34.26652	−33.72357		−6.40833	−1.55757	0.54297
6	−40.67566	−40.19574	−40.67565	−40.19577		−6.40914	−1.56445	0.47992
7	−47.08534	−46.65015				−6.40968	−1.56951	0.43519
8	−53.49530	−53.09317				−6.40996	−1.57339	0.40213
9	−59.90542	−59.52852				−6.41012	−1.57646	0.37690
10	−66.31561	−65.95847				−6.41019	−1.57894	0.35714

[a] *n* represents the number of rings. [b]Data from ref 5. [c]Direct diagonalization of the Kekulé subspace, data from ref 9. [d]$N = 4n + 2$ represents the number of C atoms.

TABLE 4: Ground-State and First Excited State Energies (in Units of *J*) of Pph as a Comparison of the DMRG Method (m = 256) with Other Methods

n[a]	E_S(DMRG)	E_T(DMRG)	E_s(exact)[b]	E_T(exact)[b]	E_0(K)[c]	ΔE_s	E_s/N[d]	$\Delta E_{S\rightarrow T}$
3	−21.52250	−20.64475	−21.52250	−20.64475	−20.52479		−1.53732	0.87775
4	−27.99497	−27.21658	−27.99497	−27.21658		−6.47247	−1.55528	0.77839
5	−34.47083	−33.75244	−34.47083	−33.75256		−6.47586	−1.56686	0.71839
6	−40.94598	−40.27229	−40.94598	−40.27243		−6.47515	−1.57485	0.67369
7	−47.42142	−46.78028				−6.47544	−1.58071	0.64114
8	−53.89681	−53.28083				−6.47539	−1.58520	0.61598
9	−60.37223	−59.77591				−6.47542	−1.58874	0.59632
10	−66.84771	−66.26700				−6.47548	−1.59161	0.58071

[a] *n* represents the number of rings. [b]Data from ref 5. [c]Direct diagonalization of the Kekulé subspace, data from ref 9. [d]$N = 4\,n + 2$ represents the number of C atoms.

the first excited state, respectively. When the retained states are increased to 256 or 512, the numerical deviations decrease to 10^{-5} *J* for the ground states and 10^{-4} *J* for first-triplet states, respectively, which is better than those obtained from other approximate schemes, for example, the ground-state energy of anthracene and naphthalene cited in the fifth column of Table 3 with errors of 1−2 *J*.[8] In most chemical problems, the energy calculation with an error of 10^{-3} to 10^{-5} *J* will be satisfactory. Therefore, considering the efficiency and quality, 256 states are used for giving the results discussed below.

3.2. Energy of Ground State. Figure 1 displays the plots for the average energy per electron of the ground state of Pac and Pph against the number of hexagons in the benzenoids on the basis of the results of the seventh column in Tables 3 and 4. Both converge as the chain length increases. The energy curve of Pph being always beneath that of Pac is consistent with the well-known fact of the higher thermal stability of Pph relative to Pac.[26]

To find how the ground-state energy varies with the chain length of PAHs, we define $\Delta E_s = E_s(n) - E_s(n-1)$ (where *n* represents the number of hexagons in the benzenoids), the increment of ground-state energy between two neighboring members for the homologous series, which are listed in the sixth column of Tables 3 and 4. Plots of ΔE_s against the chain length are shown in Figure 2. Although ΔE_s of Pac are less negative than Pph, they all decrease negligibly in proportion to the chain length, in particular, when *n* exceeds 8. On the basis of numerical data of Tables 3 and 4 and Figure 2, we derive the simple formulas for evaluating the ground-state energy (in units of *J*) of these two series, respectively.

$$E_s = -2.2137 - 6.4102n \text{ (Pac)} \tag{10}$$

$$E_s = -2.0936 - 6.4754n \text{ (Pph)} \tag{11}$$

From the formulas above, one could deduce the ground-state energy per electron of Pac and Pph at infinite chain length, equaling −1.6025 *J* and −1.6189 *J*, respectively. In addition, our calculation on polyene leads to the $E_s(n = \infty) = -1.3862$ *J*, reproducing other reports.[10,11,27] These numerical data can provide valuable information for the transition from molecules to solids.

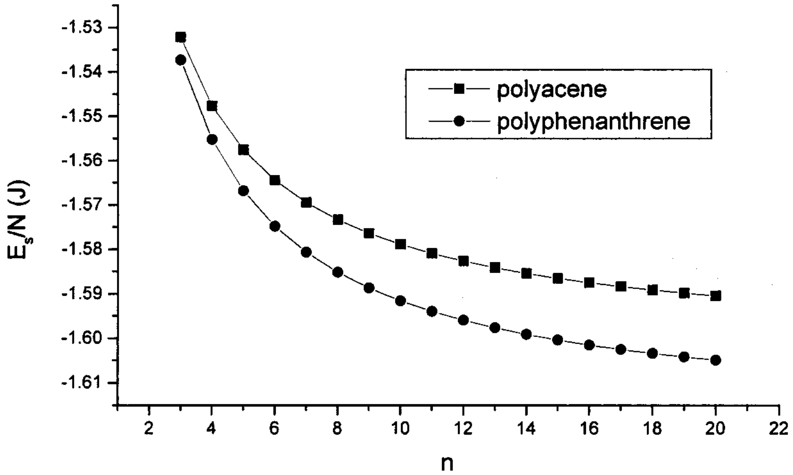


Figure 1. The average ground energy per electron vs chain length.

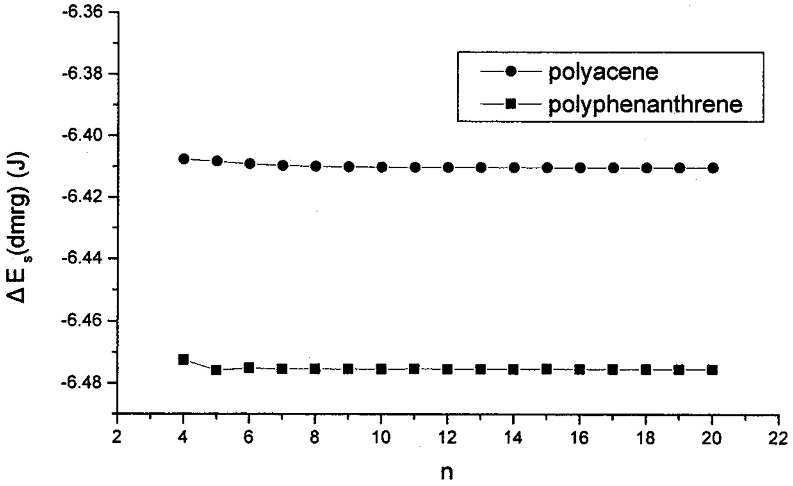


Figure 2. The increment of ground-state energy per unit length vs the chain length.

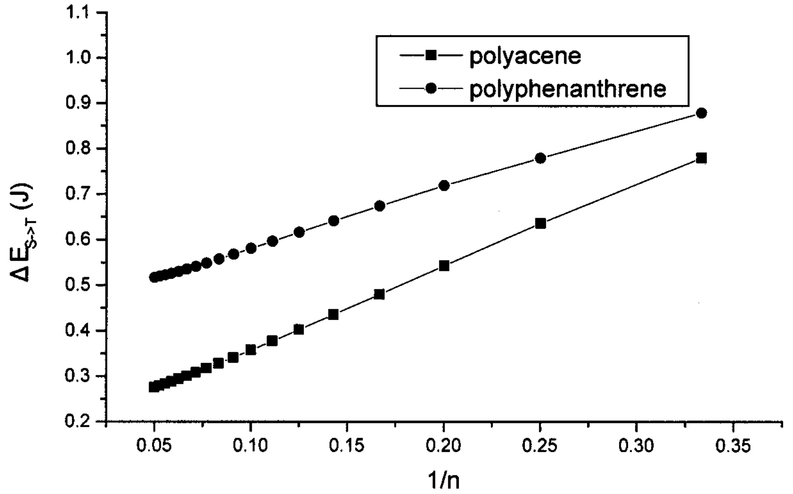


Figure 3. The energy gap of the ground state and the first excited state versus 1/*n* (*n* represents the number of the six-membered rings).

3.3.The Singlet−Triplet Energy Gap (S−T Gap). The energy gap between the ground state and the first triplet state measures the kinetic stability of the compound, and it is also an important index to be able to correlate with the reactivity of the system. In past years, considerable interest existed in polyacene as a potential one-dimensional organic conductor with a zero-band gap predicted from the single-electronic theory.[28−35] Meanwhile, because long-chain polyacenes are too active to be isolated in experiments, more calculations and extrapolations based on many-body theoretical models are necessary to explore the electronic structures of the homologous systems.[36] Just like Malrieu and co-workers had done in the study of polyene,[23b] we also use the linear and binomial equations to correlate the S−T gap with 1/*n* for both species, as shown in Figures 4 and 5, respectively. Obviously, the linear correlations are inaccurate and inadequate. The binomial equation gives better correlations for both species. We also find that the function $A + B(1/n)^x$ gives even better prediction of the S−T gaps for larger oligomers

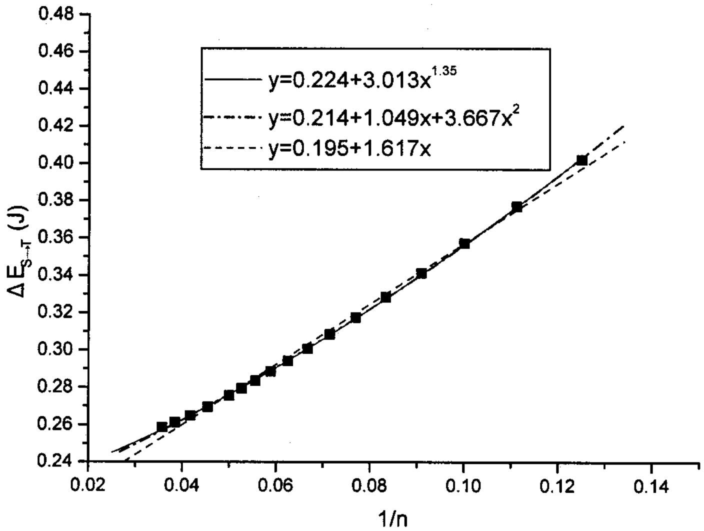


Figure 4. S−T gap vs 1/*n* (*n* represents the number of the ring member) with different correlations for Pac.

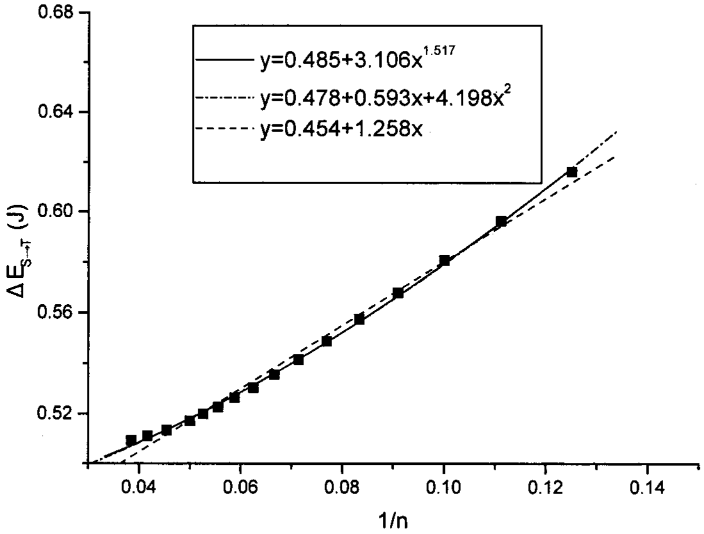


Figure 5. S−T gap vs 1/*n* (*n* represents the number of the ring member) with different correlations for Pph.

such as *n* reaches100. We would prefer to use this function, and the optimized values of *x* are determined to be 1.360 for Pac and 1.517 for Pph, respectively. According to these equations listed in Figures 4 and 5, the S−T gaps are 0.224 *J* for infinite Pac and 0.485 *J* for Pph.

By means of the measured S−T energy gaps of 1.26 eV and 2.49 eV for naphthacene[37] and picene[38] which are the largest species for Pac and Pph characterized until now, the values of *J* are determined as 1.99 eV and 3.47 eV, respectively. These values are in agreement with those published previously.[39] On adopting the numerical value of *J* above into the results of the Pac and Pph series, the values of S−T gaps at the infinite chain length can be derived to be 0.446 eV and 1.683 eV for Pac and Pph, respectively. It is also in accordance with the evidence that the Pac is significantly more reactive than Pph.[35]

3.4. Relative Hexagon Energy. Clar's sextet concepts have been well investigated by various quantum chemical calculations.[5,23,40−45] The RLHE calculated from the VB model can be used to interpret the individual benzene character for the hexagons of PAHs.[5,46−54] Here, we show 1000·RLHE of the cata-condensed benzenoids in Figure 6. In very recent articles, RLHE decreases toward the central ring of the short condensed chain.[5,47] Does the RLHE approach to a limit as Pac and Pph propagate? This is really the case as shown in Figure 6 where RLHE converges to a constant value when the chain length of Pac and Pph exceeds 12. The effective conjugated length is predicted to be 12 for the monodisperse Pac and Pph according to our DMRG calculations toward additions.

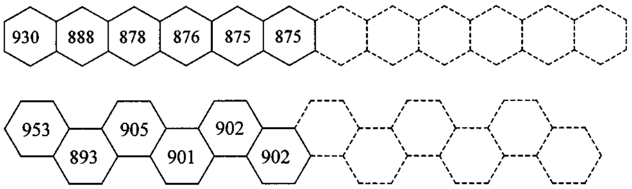


Figure 6. Convergence of 1000·RLHE values in long-chain Pac and Pph.

4. Conclusion

Long-chain PAHs are difficult to characterize experimentally, because they hardly melt and dissolve. Therefore, the electronic structures and properties were mainly studied by extrapolation of the results of oligmeric molecules. As demonstrated above, through careful selection of the starting and propagating blocks, the DMRG method will give very precise results for the ground and first excited states. In fact, DMRG can be used to compute any state by forming the density matrix according to that state.

At the same time, we could obtain the RLHEs by iterative DMRG scheme as accurately as those obtained from the exact solutions of the VB Hamiltonian. This implies that the eigenfunctions of DMRG are also well behaved and are usable to derive physical properties via enumeration of the approximate matrix elements.

The DMRG method is efficient and powerful for implementing the many-electron models for long-chain polymers, which will enrich our knowledge of the transition area from molecules to solids.

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